



**Polychlorinated Dibenzo-*P*-Dioxins
and Dibenzofurans
in Upper Columbia River
Suspended Particulate Matter, 1990-1994**

December 1997

Publication No. 97-342
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Suspended Particulate Matter, 1990-1994**

by
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December 1997

Water Body No. WA-CR-9010 (Segment No. 26-00-04)

Publication No. 97-342
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Abstract

We analyzed polychlorinated dibenzo-*p*-dioxin (PCDD) and dibenzofuran (PCDF) concentrations in suspended particulate matter (SPM) collected from the Columbia River at Northport during 1990, 1992, 1993, and 1994 autumn low-flow conditions. The primary objective was to document the effects of pollution abatement efforts by the Celgar pulp mill in Castlegar, British Columbia, 46 river miles upstream of Northport. We also estimated PCDD/PCDF loads in the river and compared the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) loads to the target for the watershed north of the international boundary as detailed in EPA's total maximum daily load (TMDL) for the Columbia River basin.

Concentrations of 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF), the major congener detected, decreased by two orders of magnitude; and the daily 2,3,7,8-TCDF load in Columbia River SPM decreased 300-fold from 1990 to 1994. The decline in 2,3,7,8-TCDF concentrations agreed well with improvements and discharge reductions reported by Celgar. 2,3,7,8-TCDD, the most toxic congener, was not detected in any samples at quantitation limits ranging from 0.4 to 1.8 pg/g. *Maximum possible* 2,3,7,8-TCDD loads in SPM were 0.5 mg/day or less, much lower than the watershed target specified in the TMDL (2.3 mg/day). By estimating dissolved 2,3,7,8-TCDD concentrations, we calculated the total *maximum possible* 2,3,7,8-TCDD loads were about one-half the watershed target in 1990 and 1994, and slightly above the target load in 1992 and 1993.

Toxicity equivalent (TEQ) concentrations, the PCDD/PCDF-associated toxicity expressed as equivalent concentrations of 2,3,7,8-TCDD, decreased seven-fold and the daily TEQ load decreased sixteen-fold from 1990 to 1994. These declines were due mainly to lower 2,3,7,8-TCDF concentrations. Congener profiles changed from year to year, yet aside from 2,3,7,8-TCDF, there was no clear trend in concentrations of SPM-bound PCDDs/PCDFs. We do not have an explanation for the shifting congener patterns but there is little evidence that it was directly related to Celgar discharges.

We recommend additional rounds of SPM collection to verify the findings of this study, check for the presence of 2,3,7,8-TCDD, and determine if sediment resuspension during high-flows contributes significant PCDD/PCDF loads to the Columbia River. Further monitoring should also include analysis for dissolved PCDDs/PCDFs.

Acknowledgments

- ◇ Sample handling and analysis was placed in the capable hands of Myrna McIntosh, Sally Cull, Debbie Lacroix, Aileen Smith, Karin Fedderson, Stuart Magoon, and Will White of the Ecology Manchester Laboratory, for which we are thankful.
- ◇ We are also grateful to Jim McLaren of the Celgar Pulp Co. for providing a tour of the Castlegar plant and explaining the many details of pulp production.
- ◇ Todd Vilen of Triangle Laboratories, Inc. provided valuable information on dioxin analysis.
- ◇ Larry Goldstein reviewed the report, and Joan LeTourneau formatted the final report.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are compounds formed during combustion of materials containing chlorinated organics, as trace contaminants in chemical production, and as unintended by-products of industrial processes such as chlorine bleaching of wood pulp. Much study and attention has been given to PCDDs/PCDFs in the upper Columbia River and Lake Roosevelt after it was discovered that chlorine-bleaching kraft pulp mills may be a significant source of these chemicals (Amendola, 1987; EPA, 1988). Concerns about the presence of PCDDs/PCDFs in the aquatic environment are due to their toxicity to a variety of organisms, environmental persistence, and tendency to bioaccumulate, especially in fish.

There are 210 PCDD/PCDF congeners, of which 17 are considered toxic. The most toxic and widely studied of these is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), often referred to as dioxin. 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) is probably the most important congener in the vicinity of bleached kraft pulp mills due to its pervasiveness and toxicity (one-tenth that of 2,3,7,8-TCDD). Other PCDDs/PCDFs, including 2,3,7,8-TCDD, may be found in the aquatic environment near pulp mills, but generally at much lower concentrations than 2,3,7,8-TCDF.

PCDD/PCDF contamination in the upper Columbia River was first documented by Environment Canada when they reported very high 2,3,7,8-TCDF concentrations in lake whitefish (*Coregonus clupeaformis*) and bottom sediments downstream of the Celgar bleached kraft pulp mill in Castlegar, British Columbia, which has operated on the banks of the Columbia River since 1960 (Figure 1) (Mah *et al.*, 1989). The Washington State Department of Ecology (Ecology) responded by conducting a reconnaissance survey to determine if PCDDs/PCDFs were detectable in Lake Roosevelt fish, findings of which indicated that further sampling was warranted (Johnson, 1990).

These surveys provided the impetus for subsequent investigations of PCDDs/PCDFs in the upper Columbia River and Lake Roosevelt (B.C. Ministry of Environment, 1990; Johnson *et al.*, 1991a,b,&c; Boyle *et al.*, 1992; Serdar *et al.*, 1993 & 1994). Most of these investigations have focused on residues in fish in order to assess human health risks. Although a discussion of the fish data is beyond the scope of this report, it is noteworthy that contamination of certain species was at one time substantial enough to elicit consumption advisories on both sides of the border (Kirkpatrick, 1989; Gebbie, 1990).

Ecology first analyzed suspended particulate matter (SPM) from the Columbia River at Northport in 1990 as a way to estimate PCDD/PCDF concentrations in the water column (Johnson *et al.*, 1991c). Because of their tendency to sorb to sediments, PCDDs/PCDFs are readily detectable in SPM compared to analysis of whole water. The SPM data were used in turn to estimate PCDD/PCDF loads to Lake Roosevelt and assist Ecology's Water Quality Program and the U.S Environmental Protection Agency

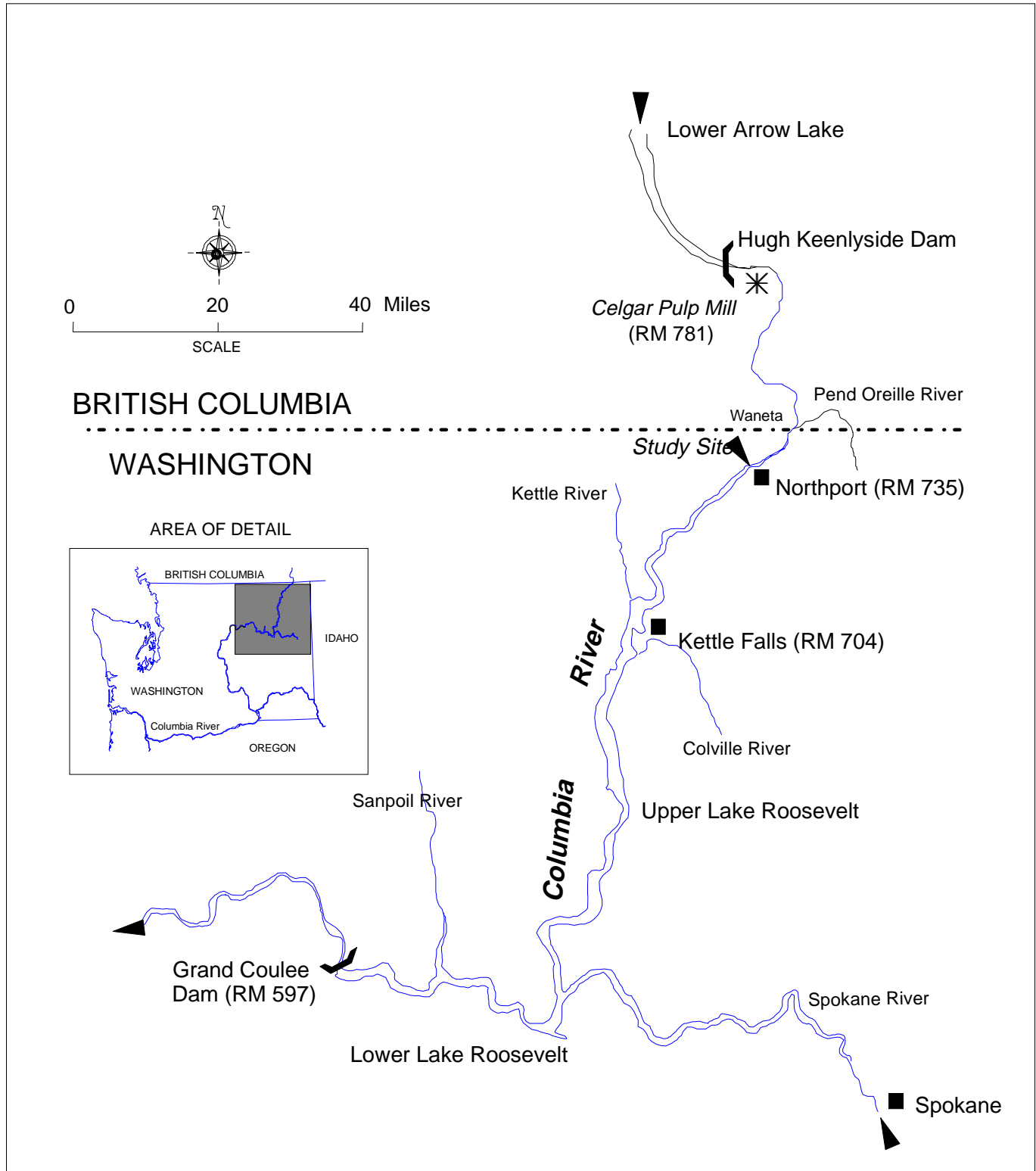


Figure 1. Location of the Northport Study Site and the Upper Columbia River

(EPA) in refining the Columbia River total maximum daily load (TMDL) to limit the discharge of 2,3,7,8-TCDD to the Columbia River basin. The TMDL, finalized by EPA in 1991, identifies a loading capacity or watershed target of 2.31 mg 2,3,7,8-TCDD/day for the Columbia River north of the international boundary (EPA, 1991).

Celgar Expansion and Modernization

In 1991, the Canadian federal government and British Columbia provincial government approved an expansion and modernization plan for the mill to be completed by July 1, 1993. In addition to more than doubling its pulp output to 1200 air-dried tonnes per day, the plan called for process changes and secondary wastewater effluent treatment (previously discharged to the Columbia River untreated) which were expected to reduce PCDDs/PCDFs in Celgar's final effluent to undetectable levels (Celgar Expansion Review Panel, 1991). Celgar also reported more immediate pollution reductions in 1991, including increased substitution of chlorine dioxide for chlorine in pulp bleaching, use of hydrogen peroxide in the delignification process, and removal of recovery boiler scrubber water which contained dibenzofuran, a PCDF precursor.

Ecology's Trend Monitoring Program

With the news of ongoing and planned improvements at Celgar, Ecology decided to conduct long-term monitoring in the upper Columbia River and Lake Roosevelt. EPA provided Ecology with a Clean Lakes grant to initiate contaminant monitoring during 1992-1993. The primary goal of the trend monitoring was to document the effects of pollution controls being implemented by Celgar, as well as the Cominco smelter¹.

To achieve this goal, Ecology decided to build upon the data collected during 1990 as a basis for continued monitoring of PCDDs/PCDFs. Among the sample media analyzed during 1990, SPM and lake whitefish tissues were selected for trend monitoring mainly due to their elevated concentrations of 2,3,7,8-TCDF, and to a lesser extent, 2,3,7,8-TCDD in whitefish. SPM was viewed as a useful gauge of instantaneous PCDDs/PCDFs levels in the water column and concurrent discharges by Celgar. Lake whitefish, on the other hand, were considered useful for longer-term monitoring due to their accumulation of these persistent compounds over time.

¹Cominco Ltd. operations in Trail, B.C., located on the banks of the Columbia River approximately 11 river miles above the international boundary, include the world's largest integrated lead-zinc smelter and refinery. It is considered to be the major source of metals contamination in the upper Columbia River and upper Lake Roosevelt. Ecology's monitoring program also included collection of data to analyze trends in metals contamination. The metals data are included in Serdar *et al.*, (1993 & 1994) and several forthcoming Ecology reports.

Measurable trends in whitefish 2,3,7,8-TCDF and 2,3,7,8-TCDD concentrations were not expected for several years. However, improvements at Celgar were translated into significant declines of these compounds in muscle tissues between 1990 and 1993 (Serdar *et*

al., 1994). For instance, 2,3,7,8-TCDF in whitefish muscle decreased from a mean concentration of 126 pg/g (parts per trillion) in 1990 to 62 pg/g in 1992, then declined further to 33 pg/g in 1993. There was also a four-fold decrease in 2,3,7,8-TCDD concentrations, with most of the decline occurring between 1990 and 1992. Analysis of whitefish tissues by Ecology was dropped subsequent to 1993 to avoid duplicating part of an EPA survey of PCDDs/PCDFs in Lake Roosevelt fish during 1994.

Results of previous monitoring for PCDDs/PCDFs in the upper Columbia River and Lake Roosevelt have been reported in *Interim Report on Monitoring Contaminant Trends in Lake Roosevelt* (Serdar *et al.*, 1993) and *Contaminant Trends in Lake Roosevelt* (Serdar *et al.*, 1994). A more detailed analysis of samples collected during 1990 may also be found in *PCDDs/PCDFs in Columbia River Suspended Particulate Matter* (Johnson *et al.*, 1991c) and *Polychlorinated Dioxins and -Furans in Lake Roosevelt (Columbia River) Sportfish* (Johnson *et al.*, 1991a).

Objectives

The present report contains results of monitoring PCDDs/PCDFs in SPM during 1990-1994.

The objectives were to:

- Document the effects of pollution controls instituted by Celgar.
- Estimate PCDD/PCDF loads in the Columbia River at Northport and to Lake Roosevelt downstream.
- Compare the 2,3,7,8-TCDD load to the target load for the Columbia River watershed north of the international boundary, as detailed in EPA's TMDL for the Columbia River basin.

Methods

Site Selection

We selected Northport (Figure 2) as a sampling site because it is an accessible, free-flowing reach of the river upstream of the large depositional areas (*i.e.*, PCDD/PCDF sinks) in Lake Roosevelt (Johnson *et al.*, 1991b). At Columbia River mile 735, Northport is approximately 10 river miles below the international border and 46 river miles below Celgar. Samples were collected off a man-made gravel bar extending into the Columbia River from the left bank, near the Northport boat launch.

The reach between Northport and the international border is in a relatively natural state. Aside from a few houses and a two-lane highway, there is little development along the banks. The substrate is sandy, with gravel and cobble-sized material in riffle areas; there is very little fine material (≤ 0.062 mm) in the sediments (Johnson *et al.*, 1988). The watershed of the border reach is primarily forested, with several small tributary streams. The Pend Oreille River enters the Columbia on the left bank just north of the Canada border, contributing 27% of the mean annual Columbia River flow at the border (Butcher, 1992).

Sample Collection

Sampling of Columbia River SPM in 1990, 1992, 1993, and 1994 was conducted in a nearly identical manner. For all years, a three-day composite sample was collected during low river flow in late September or early October.

River water was pumped from an intake situated in 12-ft deep water (5-ft in 1990) approximately 50 feet offshore in the main current of the river. The depth of the intake was periodically adjusted to 2, 5, and 10-ft depths (1 and 4-ft in 1990) to approximate a depth-integrated sample. The water was delivered via a peristaltic pump to two Alfa-Laval Sedisamp II continuous-flow centrifuges (model 101IL) which extracted SPM from whole water.

To avoid sample contamination, all surfaces coming in contact with the samples were pre-cleaned by scrubbing with Liquinox® detergent, followed by sequential rinses with hot tap water, nitric acid (except 1990), de-ionized water, acetone, and hexane. Tubing and fittings were Teflon® or Teflon-lined except for Silastic® tubing on the peristaltic pump. Nalgene® tubing was used for the intake line in 1994. Centrifuge bowl parts are constructed of high quality stainless steel.

Table 1 compares the flow rate, centrifuge run time, amount of sample obtained, SPM removal efficiency, and Columbia River flow among years. The centrifuge removal efficiency is based on data from laboratory analysis of total suspended solids (TSS) in

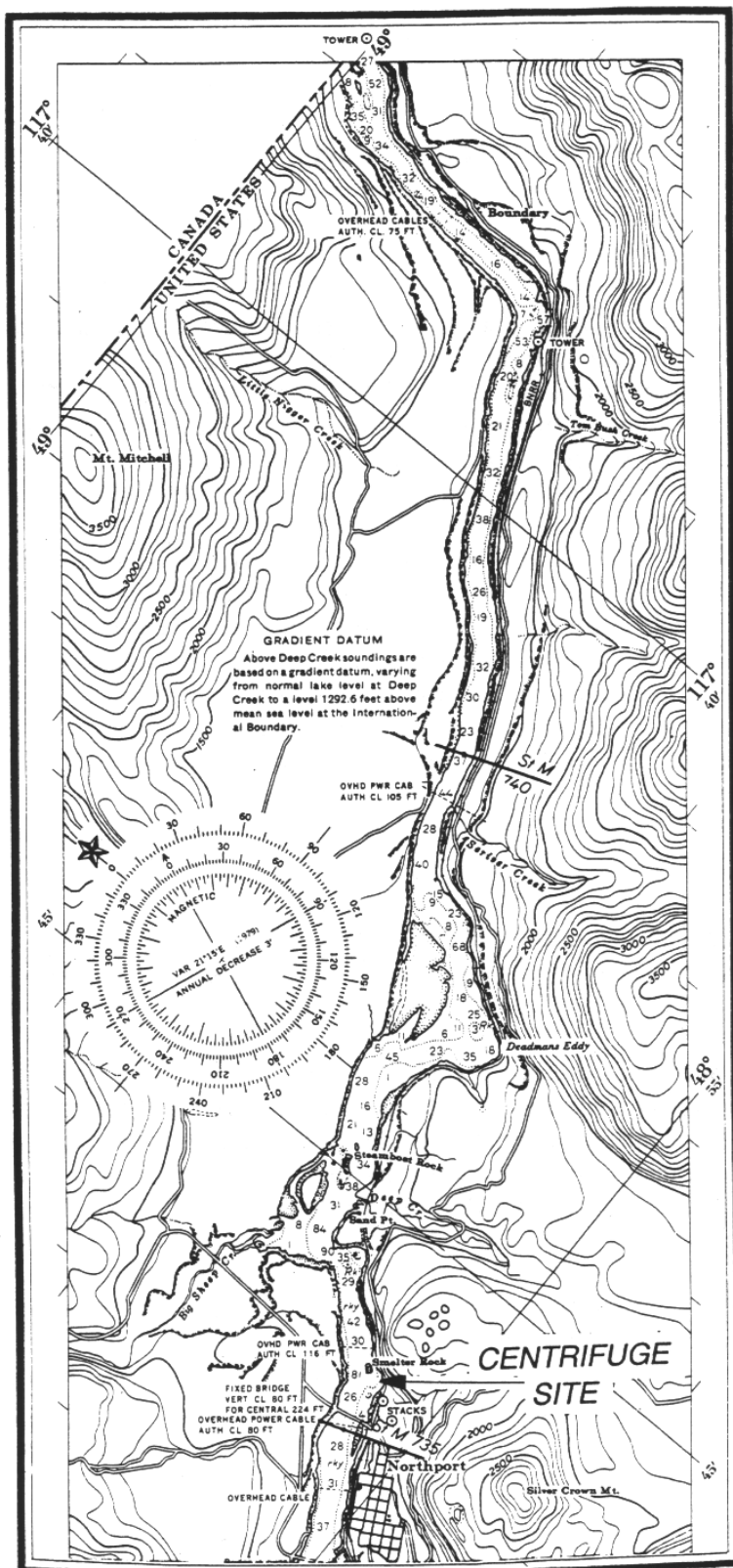


Figure 2. SPM Sampling Site

water samples and from pump-flow measurements. Flow data were obtained from the U. S. Geological Survey NASQAN Station 12399500 (Columbia River @ International Boundary).

Table 1. SPM Sample Collection Parameters, 1990-1994.

	1990 (Oct 9-11)	1992 (Sep 29-Oct 2)	1993 (Oct 5-7)	1994 (Oct 10-12)
Average combined flow rate to centrifuges (L/h)	270	170	170	330
Centrifuge run time (h)	57	59	68	57
Volume of water centrifuged (L)	15,450	10,200	11,540	18,925
Amount of SPM obtained (g, wet)	90	68	81	97
% Solids	26.2	21.2	16.4	16.0
Dry weight of sample (g)	23.6	14.4	13.3	15.5
SPM removal efficiency (%)	76	100	61	unknown
Average flow at border (m ³ /s)	1,745	2,662	1,628	1,689

SPM accumulated by the centrifuge was scraped from the centrifuge bowl with a Teflon-coated spatula and placed in amber glass jars specially cleaned for trace organics analysis. Water samples were also collected at eight to fourteen hour intervals for analysis of specific conductance, total organic carbon (TOC), dissolved organic carbon (DOC), TSS, pH, and temperature. Samples for DOC were not analyzed in 1990. Water samples for TOC and DOC analysis were preserved with sulfuric acid to pH<2. DOC samples were filtered with a 0.45 µm extraction disc in the field prior to acidification. Measurements of pH and temperature were done in the field. All samples for laboratory analysis were kept on ice while in the field.

Sample Analysis

SPM samples were analyzed for all 2,3,7,8-substituted PCDDs and PCDFs using isotope dilution, high resolution GC/MS EPA Method 8290 or 1613. SPM samples from 1990, 1992, and 1993 were analyzed using EPA 8290 by: Alta Analytical Laboratory in El Dorado Hills, CA (1990); Enseco California Analytical Laboratory in West Sacramento, CA (1992); and Triangle Laboratories in Research Triangle Park, NC (1993). The 1994 sample was analyzed by Pacific Analytical in Carlsbad, CA using EPA 1613.

Methods 8290 and 1613 have minor differences with respect to the use of internal standards (1613 requires more), reporting of estimated maximum possible concentrations (EMPCs; 1613 does not report these), calibration range (1613 is twice as wide), and

laboratory control samples (1613 requires one at the beginning of each instrument run). Their use may be dictated more by laboratory preference than actual performance (personal communications with Dante Bencivengo, Pacific Analytical and Todd Vilen, Triangle Laboratories). We found no evidence to indicate that either method generates biased data or would otherwise preclude data comparability among years.

TOC and percent solids determination in the SPM sample were done by Puget Sound Estuary Program protocols (EPA, 1986a) and EPA Method 160.3, respectively. Analysis of water samples was conducted according to the following EPA methods: specific conductance - EPA 120.1; TOC and DOC - EPA 415.1; and TSS - EPA 160.2.

Data Quality

Complete results of PCDD/PCDF analyses for each year are in the Appendix. Stuart Magoon of the Manchester Environmental Laboratory reviewed all of the PCDD/PCDF data for holding times, method blanks, initial and continuing calibration, internal standard recoveries, isotopic abundance ratios, and matrix spike recoveries.

Overall quality of the data was good. SPM samples collected during 1990 and 1992 were analyzed in duplicate for all seventeen 2,3,7,8-PCDDs/PCDFs to assess precision. The size of the 1994 sample was not sufficient to analyze in duplicate, and the 1993 sample was large enough to conduct duplicate analysis of 2,3,7,8-TCDD and 2,3,7,8-TCDF only. For samples analyzed in duplicate, the relative percent difference (range as a percent of the mean) was generally less than 30%. Duplicate analysis of matrix spikes also showed good precision.

For the most part, analyses of PCDDs/PCDFs were within the method quality control limits and all data are useable as qualified. Qualifiers were included in the following instances:

- Some of the 1992 and 1994 results were below the lower calibration limit and were therefore qualified as estimates (J).
- Analysis of four PCDDs/PCDFs in 1993 did not meet Method 8290 criteria for isotopic abundance ratios. Results were qualified as estimated maximum possible concentrations (EMPCs).
- Two other analytes from the 1993 sample were below practical quantitation limits and were qualified as estimates (J).
- 2,3,4,6,7,8-HxCDF was detected in the 1993 method blank at a concentration equal to 38% of the analytical result. 2,3,7,8-TCDD was detected in the 1994 method blank at a concentration equal to 28% of the analytical result. The presence of these analytes were therefore considered results of laboratory contamination and not native to the samples (UJ).

- The internal standard for OCDD in 1994 was below the acceptable recovery limit (J).

Results

General Water Quality Characteristics of the Columbia River at Northport

Table 2 shows results of water sample analysis. Specific conductance and temperature showed little variation within or among years. The TOC levels in 1990 were about double that in following years, and pH varied substantially among years. While we cannot explain the relatively high TOC in 1990, differences in sampling practices may explain the variations in pH. Higher pH values were obtained during 1990 and 1994 when samples were taken *in situ*, and are more consistent with historical records of pH in the upper Columbia River (USGS, 1980-1991). When samples were taken from the centrifuge intake manifold, as in 1992 and 1993, the pH values were much lower. We conclude that the pressure differential caused by pumping the sample approximately 200 feet horizontally and 20 feet vertically caused changes in dissolved gas concentrations which in turn resulted in lower pH.

Table 2. Summary of Columbia River Water Quality at Northport During SPM Sample Collection (mean \pm SD).

	1990 (n=8)	1992 (n=7)	1993 (n=6)	1994 (n=6)
Specific Conductance (μ mhos/cm)	148 \pm 2	135 \pm 2	150 \pm 3	140 \pm 4
Total Organic Carbon (mg/L)	3.3 \pm 0.1	1.3 \pm 0	1.9 \pm 0.2	1.4 \pm 0.1
Dissolved Organic Carbon (mg/L)	na	1.1 \pm 0.1	1.9 \pm 0.6	1.3 \pm 0.1
Total Suspended Solids (mg/L)	2.0 \pm 0.5	1.4 \pm 0.5	2.2 \pm 0.4	0.8 J
pH (s.u., median value)	8.2	7.2	6.9	8.3
Temperature (C)	13.0 \pm 0.6	14.7 \pm 1.0	14.5 \pm 1.0	15.1 \pm 0.5

na=not analyzed

J=estimated value

TSS concentrations obtained during 1994 were lower than normal; four of the six water samples had concentrations below the laboratory's reporting limit of 1 mg/L. The 0.8 mg/L value shown in Table 2 was calculated by dividing the dry weight of the SPM sample by the volume of water centrifuged. Since reliable TSS values were not obtained from laboratory analysis, there is no way to assess the centrifuge's SPM-removal efficiency, which had been estimated to range from 60-100% during previous years of monitoring (Table 1).

As a result of low TSS concentrations in 1994, the estimated daily load of suspended solids in the Columbia River at Northport was also much lower than during previous monitoring. Estimates of daily suspended solids loads during 1990-1993 monitoring had been consistent among years, ranging from 300,000 to 320,000 Kg/day. The daily suspended solids load during the 1994 monitoring was approximately 117,000 Kg/day.

2,3,7,8-PCDD/PCDF Concentrations in Suspended Particulate Matter

PCDD/PCDF concentrations in SPM samples obtained during 1990-1994 are shown in Table 3. The samples collected during 1993 and 1994 had more organic carbon and slightly more moisture than in previous years. This may be due to the relative absence of silt-sized slag particles originating from the Cominco smelter, which had previously been observed as a major component of SPM (Bortleson *et al.*, 1994). The odor and texture of the 1993 and 1994 samples suggest that it contained a greater proportion of biological material than previous samples.

Six PCDDs/PCDFs were detected in the 1990 SPM sample, three in 1992, fourteen in 1993, and nine in 1994. The small number of PCDDs/PCDFs found in the 1992 sample was probably due to relatively high detection limits. Of the 17 PCDD/PCDF congeners analyzed, all but one – 1,2,3,7,8,9 HxCDF – were detected in at least one of the SPM samples. OCDD, 1,2,3,4,6,7,8-HpCDD, and 2,3,7,8-TCDF were generally found at the highest concentrations and were the only congeners detected all four years. Other PCDDs/PCDFs were detected at low concentrations (less than 5 pg/g) in all but two instances.

2,3,7,8-TCDF was detected in the 1994 SPM sample at 1.1 pg/g. This represents a 75% decrease from the 1993 concentration and is two orders of magnitude lower than in 1990. 2,3,7,8-TCDD was not detected in SPM during 1990, 1992, or 1993 at quantitation limits ranging from 0.4 to 1.7 pg/g. 2,3,7,8-TCDD was detected in the 1994 SPM sample at 1.8 pg/g, but as mentioned previously, its presence was considered a result of laboratory contamination.

Figure 3 illustrates the variation in congener composition from year to year. OCDD, and to a lesser extent 1,2,3,4,6,7,8-HpCDD, became the predominant congeners during 1992-1994 after 2,3,7,8-TCDF concentrations dropped precipitously from the 1990 level. However, concentrations of these PCDD congeners also dropped dramatically – 20 to 30-fold – between 1993 and 1994.

Table 3. Concentrations of 2,3,7,8-PCDDs/PCDFs in Columbia River SPM at Northport, 1990-1994 (mean \pm range; pg/g [parts per trillion], dry weight basis).

Compound	TEF	1990 (n=2)	1992 (n=2)	1993 (n=2)*	1994 (n=1)
% Moisture		73.8	78.8	83.6	84.0
% TOC		7.6	2.2	10.4	12.0
2,3,7,8-TCDD	1	U(0.8-0.9)	U(1.5-1.7)	U(0.4-0.7)	1.8 UJ
1,2,3,7,8-PeCDD	0.5	U(0.5)	U(1.0-1.5)	0.5 EMPC	2.3 J
1,2,3,4,7,8-HxCDD	0.1	U(0.9-1.3)	U(2.5-2.6)	1.5	U(0.6)
1,2,3,6,7,8-HxCDD	0.1	U(0.7-1.0)	U(3.2)	3.0	U(1.2)
1,2,3,7,8,9-HxCDD	0.1	U(0.8-1.1)	U(2.7)	3.2 J	U(0.5)
1,2,3,4,6,7,8-HpCDD	0.01	11 \pm 1	31 \pm 6 J	74	3.5 J
OCDD	0.001	79 \pm 9	214 \pm 30	482	16.5 J
2,3,7,8-TCDF	0.1	99 \pm 22	6.2 \pm 0.4 J	4.4 \pm 0.2	1.1 J
1,2,3,7,8-PeCDF	0.05	1.0 \pm 0.1	U(1.7-1.8)	0.7 J	1.2 J
2,3,4,7,8-PeCDF	0.5	1.4 \pm 0.2	U(2.5-2.6)	0.6 EMPC	U(0.3)
1,2,3,4,7,8-HxCDF	0.1	U(0.2-0.4)	U(2.2-2.6)	1.3 EMPC	U(0.5)
1,2,3,6,7,8-HxCDF	0.1	U(0.2-0.3)	U(2.4-2.8)	0.6	1.0 J
2,3,4,6,7,8-HxCDF	0.1	U(0.2-0.3)	U(2.2-2.5)	1.7 UJ	0.4 J
1,2,3,7,8,9-HxCDF	0.1	U(0.3-0.4)	U(2.2-2.6)	U(0.5)	U(0.4)
1,2,3,4,6,7,8-HpCDF	0.01	U(1.1-1.7)	U(1.2-10)	8.5	1.2 J
1,2,3,4,7,8,9-HpCDF	0.01	U(0.5-0.6)	U(1.0-10)	0.9 EMPC	U(0.7)
OCDF	0.001	4.6 \pm 0.7	U(11-14)	23.6	U(1.7)
TEQ=		10.8	1.1	3.3	1.5

detected PCDDs/PCDFs in **bold** print

TEF=Toxicity Equivalency Factor

*duplicate analysis of 2,3,7,8-TCDD and 2,3,7,8-TCDF only

U=Undetected at or above range of quantitation limits in parentheses

UJ=analyte detected in method blank

EMPC=Estimated Maximum Possible Concentration

J=estimated concentration due to result below calibration range, below practical quantitation limit, or associated internal standard below recovery limit.

TEQ=Toxicity Equivalent, based on detected values

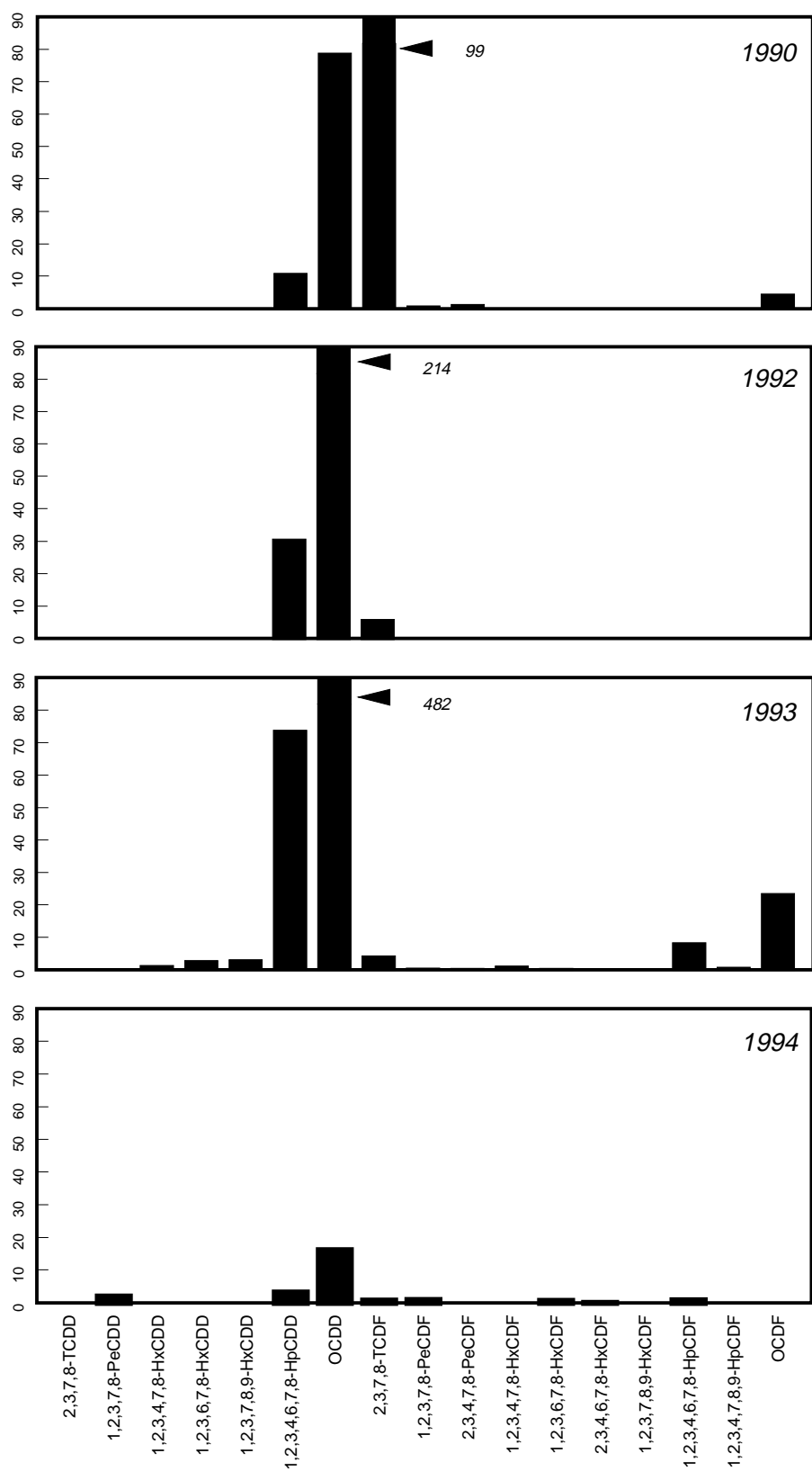


Figure 3. PCDD/PCDF Concentrations in Columbia River SPM at Northport, 1990-1994 (pg/g, dry weight basis).

Toxicity Equivalence

All seventeen PCDDs/PCDFs congeners with chlorine atoms in the 2, 3, 7, and 8 positions (*e.g.* 1,2,3,4,6,7,8-HpCDD) are considered to have a high level of toxicity, with 2,3,7,8-TCDD being the most toxic. An individual congener's toxicity relative to 2,3,7,8-TCDD, or toxicity equivalency factor (TEF), may be used to convert its concentration into an equivalent concentration of 2,3,7,8-TCDD, referred to as a toxicity equivalent (TEQ). In general, congeners with greater chlorine substitution (*e.g.* OCDF) have lower TEFs than less chlorinated congeners (*e.g.* 2,3,7,8-TCDF) (Table 3). Because PCDDs/PCDFs are generally found in mixtures, the TEQ concentration of a sample is expressed as the sum of TEQs for each congener. TEQs have no regulatory basis in water, but may be used to estimate risks associated with exposure to 2,3,7,8-PCDD/PCDF mixtures (Barnes *et al.*, 1989).

TEQs, calculated from PCDDs/PCDFs detected in SPM, declined by an order of magnitude from 1990 to 1992 (10.8 vs. 1.1 pg/g). From 1992 to 1993, TEQ increased three-fold to 3.3 pg/g, then dropped to 1.5 pg/g in 1994. At least some of the dramatic decline in TEQ from 1990 to 1992 was due to the much higher detection limits in 1992 as compared to 1990 (and other years). For instance, if non-detected congeners were used to derive the TEQ using one-half the mean detection limits, TEQs for 1990 and 1992 would be 12.3 and 6.7 pg/g, respectively (4.1 pg/g for 1993 and 2.9 pg/g for 1994).

Perhaps more interesting is the change in compounds responsible for the toxicity, as shown in Figure 4. In 1990 and 1992, the congener 2,3,7,8-TCDF accounted for 92% and 56% of the TEQ, respectively. In 1993, no single PCDD/PCDF accounted for the majority of TEQ (1,2,3,4,6,7,8-HpCDD had the greatest contribution at 22%). 1,2,3,7,8-PeCDD accounted for 75% of the TEQ in the 1994 sample. Again, these changes reflect shifting patterns in the composition and concentrations of PCDDs/PCDFs bound to suspended particulate matter.

2,3,7,8-PCDD/PCDF Loads in the Columbia River at Northport

Daily loads of SPM-bound PCDDs/PCDFs in the Columbia River at Northport were calculated for each year as the product of their concentration in SPM, TSS concentration in water, and the daily Columbia River discharge (Table 4). The PCDD/PCDF loads in Table 4 probably underestimate actual loads because they do not account for dissolved PCDDs/PCDFs. The loads detected in 1994 were generally one-to-two orders of magnitude lower than previous years due to both lower congener concentrations and suspended solids loads in the river. The 2,3,7,8-TCDF load decreased 300-fold between 1990 and 1994.

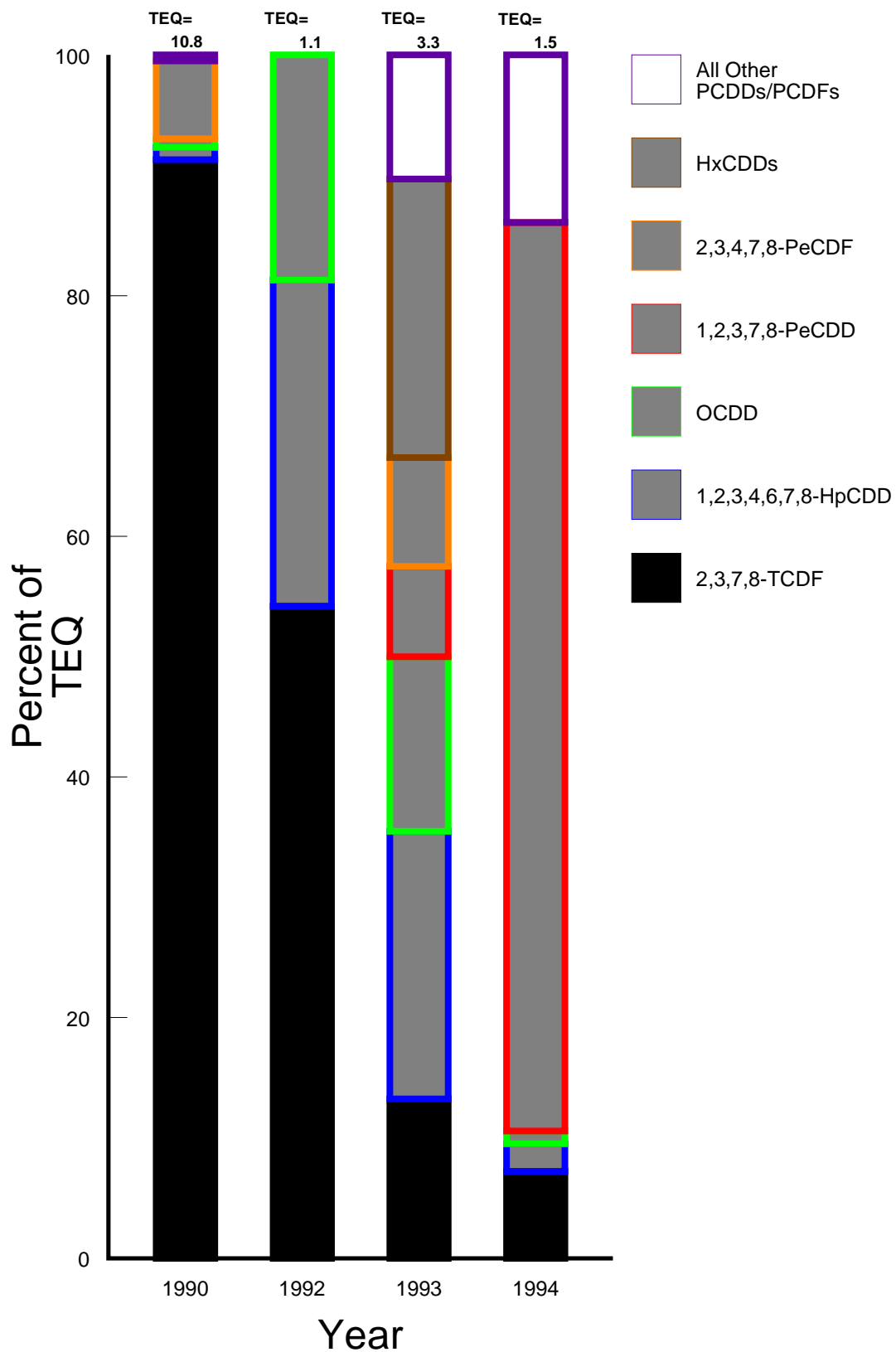


Figure 4. Contribution of PCDD/PCDF Congeners to TEQ

Table 4. Loads of SPM-Bound 2,3,7,8-PCDDs/PCDFs in the Columbia River at Northport, 1990-1994 (mg/day).

Compound	1990	1992	1993	1994
2,3,7,8-TCDD	nd	nd	nd	nd
1,2,3,7,8-PeCDD	nd	nd	0.2	0.3
1,2,3,4,7,8-HxCDD	nd	nd	0.5	nd
1,2,3,6,7,8-HxCDD	nd	nd	0.9	nd
1,2,3,7,8,9-HxCDD	nd	nd	1.0	nd
1,2,3,4,6,7,8-HpCDD	3.3	10	23	0.4
OCDD	24	69	150	1.9
2,3,7,8-TCDF	30	2.0	1.4	0.1
1,2,3,7,8-PeCDF	0.3	nd	0.2	0.1
2,3,4,7,8-PeCDF	0.4	nd	0.2	nd
1,2,3,4,7,8-HxCDF	nd	nd	0.4	nd
1,2,3,6,7,8-HxCDF	nd	nd	0.2	0.1
2,3,4,6,7,8-HxCDF	nd	nd	nd	0.05
1,2,3,7,8,9-HxCDF	nd	nd	nd	nd
1,2,3,4,6,7,8-HpCDF	nd	nd	2.6	0.1
1,2,3,4,7,8,9-HpCDF	nd	nd	0.3	nd
OCDF	1.4	nd	7.3	nd
TEQ=	3.3	0.4	1.0	0.2

nd=not detected

TEQ=Toxicity Equivalent

As mentioned previously, the daily suspended solids load at Northport during 1994 monitoring was approximately 40% of the loads measured 1990-1993. This probably also accounted somewhat for the low 1994 TEQ load. A suspended solids load in 1994 similar to those during 1990-1993 would have yielded a TEQ load of approximately 0.5 mg/day during 1994. The relatively low TEQ load in 1992 is due in part to the higher PCDD/PCDF detection limits reported for the 1992 sample.

Estimation of 2,3,7,8-TCDD Loads

2,3,7,8-TCDD is of special interest because, in addition to being the most toxic congener, it is the only PCDD/PCDF for which water quality criteria have been promulgated (EPA, 1986b). EPA has established a total maximum daily load (TMDL) for 2,3,7,8-TCDD to limit its discharge to the Columbia River basin (EPA, 1991).

Based on the harmonic mean flow of the Columbia River at the international border (1.78×10^8 L/day), EPA has determined that the loading capacity or watershed target for the Columbia River north of the border is 2.3 mg/day to avoid surpassing the water quality criterion of 0.013 pg/L (parts per quadrillion).

Since 2,3,7,8-TCDD was not detected in the SPM sample during the four years of monitoring, *maximum possible* SPM or solid phase loads were estimated by substituting quantitation limits for actual concentrations (Table 5). The highest quantitation limits were used for years where ranges are reported (1990, 1992, and 1993). Solid phase loads for all years except 1992 were approximately 0.2 - 0.3 mg/day. The higher load estimate for 1992 was due to a high quantitation limit for 2,3,7,8-TCDD.

Table 5. Estimated *Maximum Possible* 2,3,7,8-TCDD Loads and Whole Water Concentrations in the Columbia River at Northport, 1990-1994.

	1990	1992	1993	1994
Solid Phase 2,3,7,8-TCDD Load (mg/day)	0.3 ^a	0.5 ^a	0.2 ^a	0.2 ^a
Dissolved Phase 2,3,7,8-TCDD Load (mg/day)	0.9 ^b	2.3 ^c	2.3 ^d	1.1 ^b
Total 2,3,7,8-TCDD Load (mg/day)	1.2	2.8	2.5	1.3
Whole Water Concentration (pg/L)	0.008	0.012	0.018	0.009

^aBased on quantitation limits, this report

^cBased on quantitation limits, Bortleson *et al.* (1994)

^bEstimated using K_{oc} of 2.00×10^6

^dBased on quantitation limits, Serdar *et al.* (1994)

We also estimated dissolved phase loads for 2,3,7,8-TCDD (Table 5) because a potentially significant fraction is likely dissolved due to the low concentration of suspended solids in the water column. The TMDL and water quality criterion for 2,3,7,8-TCDD are based on whole water, not simply the solid phase.

Maximum possible dissolved 2,3,7,8-TCDD loads for 1992 and 1993 were based on results of sampling at Northport conducted by the U.S. Geological Survey (USGS) during 1992 (Bortleson *et al.*, 1994) and Ecology during 1993 (Serdar *et al.*, 1994). Columns packed with XAD resin were used to concentrate dissolved 2,3,7,8-TCDD in clarified river water. Neither the USGS nor Ecology detected dissolved 2,3,7,8-TCDD at quantitation limits of 0.01 pg/L and 0.016 pg/L, respectively. However, the quantitation limits are useful in estimating *maximum possible* loads, as done for SPM. *Maximum possible* dissolved loads for both 1992 and 1993 were 2.3 mg/day, yielding total (solid + dissolved loads) of 2.8 and 2.5 mg/day, respectively.

Since dissolved phase monitoring was not conducted during 1990 and 1994, we calculated theoretical dissolved loads using the 2,3,7,8-TCDD sorption partition coefficient (K_{oc}). The K_{oc} is a value derived from a hydrophobic compound's equilibrium distribution between sediment and water and normalized to organic carbon. The fraction of 2,3,7,8-TCDD in the dissolved phase can be calculated from the equation:

$$\text{Fraction of dissolved 2,3,7,8-TCDD} = \{1 + (K_{oc} \times \text{Fraction OC in SPM} \times \text{Fraction SPM in water})\}^{-1}$$

K_{oc} values are obtained experimentally, by observations of partitioning between water and solid phases with known organic carbon content, or they may be calculated using other properties of a compound, such as its relative solubility in octanol and water. Mackay *et*

al. (1992) have compiled thirty-three 2,3,7,8-TCDD K_{oc} values from the literature, derived both empirically and theoretically, and ranging from 1.15×10^3 to 3.89×10^7 with a median value of 2.00×10^6 . We used the median K_{oc} (2.00×10^6) to calculate dissolved loads.

Total *maximum possible* water column concentrations and daily loads in 1990 and 1994 were about one-half of EPA's water quality criterion and watershed target for the Columbia River north of the international border. In 1992 and 1993, daily *maximum possible* 2,3,7,8-TCDD loads were slightly higher than the target of 2.3 mg/day, although the concentration in water during 1993 was slightly below the criterion of 0.013 pg/L.

Discussion

Pollution Abatement by Celgar

The primary objective of this four-year monitoring program was to document the effects of pollution controls instituted by the Celgar pulp mill. By the time we collected our initial SPM sample in 1990 Celgar had already taken some measures to reduce their discharge of PCDDs/PCDFs, such as terminating the use of defoamers which contained PCDD/PCDF precursors and beginning to substitute chlorine dioxide for chlorine in the bleaching process. Because some of these early process changes were implemented before reliable data were available on PCDDs/PCDFs in Celgar's effluent, it is unclear to what extent they had reduced concentrations prior to 1990.

Figure 5 shows 2,3,7,8-TCDF in Celgar effluent from May 1989 through October 1994. These data, collected and reported by Celgar, indicate that the largest reductions in 2,3,7,8-TCDF discharges occurred during 1991. Celgar (1992) cites these improvements as a result of further refinements in production processes, such as increased chlorine dioxide substitution for chlorine. By the time the modernized mill and secondary treatment system were fully operational in mid-1993, 2,3,7,8-TCDF concentrations in Celgar effluent were no longer detectable at a limit of 2 pg/L (Celgar Pulp Co., 1993 & 1994; Jim McLaren, Environmental Manager, Celgar Pulp Co., personal and written communications).

Decreased concentrations and loads of 2,3,7,8-TCDF in SPM correspond well with reductions achieved by Celgar from 1990 to 1994. Until 1993, 2,3,7,8-TCDF was the most significant congener downstream of Celgar due to its contribution to overall toxicity and consistent detectability – usually at the highest concentrations. 2,3,7,8-TCDD, although more important from a toxicity and regulatory standpoint, was detected in only 15% of effluent samples analyzed by Celgar between May 1989 and October 1994.

Celgar did not begin monitoring for the full suite of 2,3,7,8-PCDDs/PCDFs until September 1992. During the following two years, they reported results on 16 effluent samples, in which OCDD was the most frequently detected (38% of samples), followed by 2,3,7,8-TCDF (19%), 2,3,7,8-TCDD (12%), and OCDF (6%). Four effluent samples were also analyzed between March 1995 and March 1996. The only PCDDs/PCDFs detected were OCDD (in all four samples) and 1,2,3,4,6,7,8-HpCDD (two samples).

There are no documented sources of PCDDs/PCDFs to the study area aside from the Celgar pulp mill. Possible point sources, although probably very small, may include several wood preservation operations and municipal wastewater treatment plants in the Pend Oreille drainage (BCI, 1991-Draft) and along the Columbia River between the border and Hugh Keenlyside Dam (Butcher, 1992; MacDonald Environmental Sciences

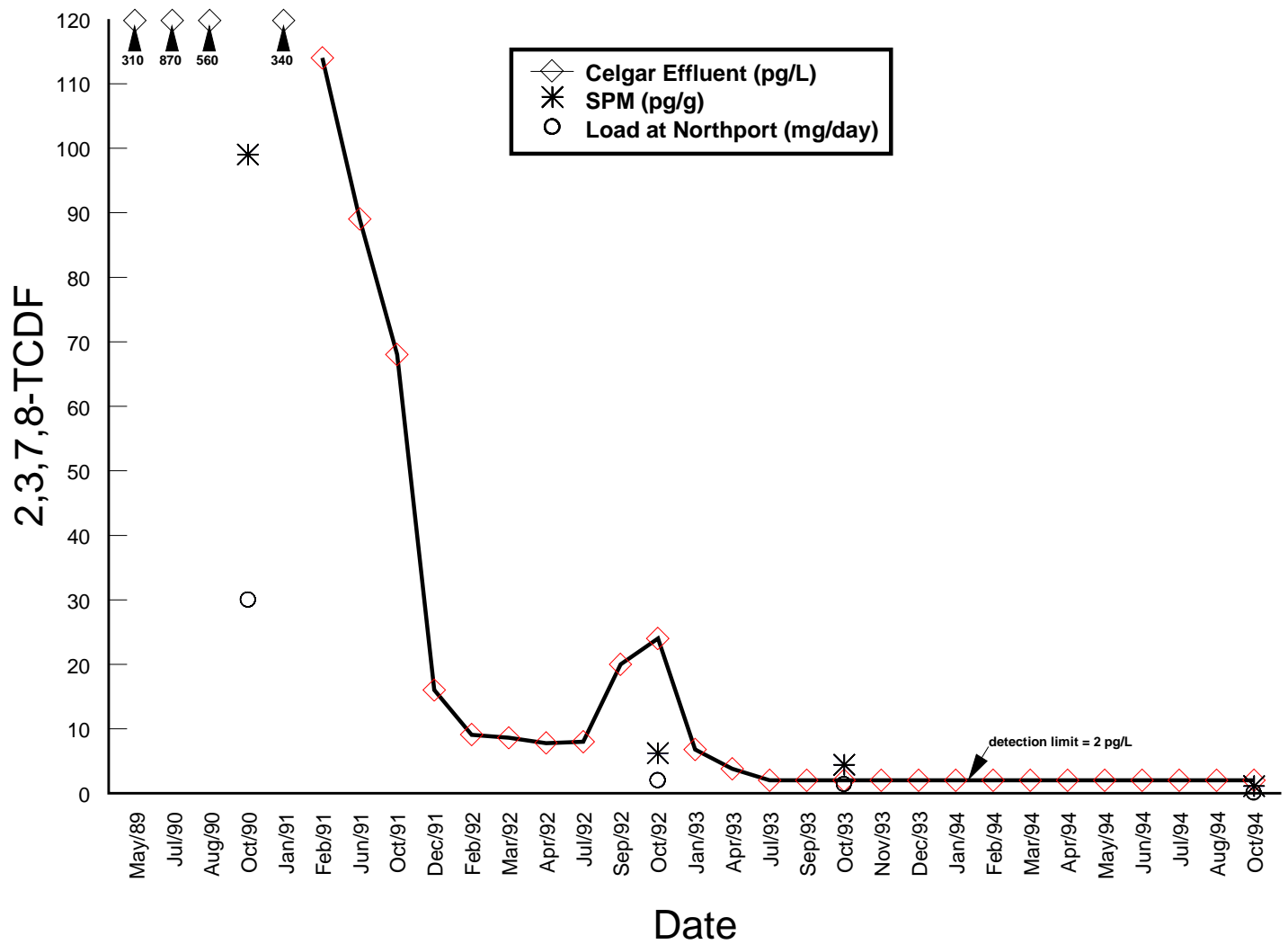


Figure 5. Concentrations of 2,3,7,8-TCDF in Celgar Effluent Plotted with Concentrations in SPM and Loads at Northport

Ltd., 1997-Draft). Celgar is probably not a continuing source of measurable PCDDs/PCDFs, with the possible exception of 1,2,3,4,6,7,8-HpCDD and OCDD.

Although there are no data to indicate a specific source of non-Celgar PCDDs/PCDFs detected in SPM, possibilities may include: 1) resuspension of contaminated bottom sediments between Celgar and Northport; 2) undocumented urban or industrial pollutant sources to the river; and 3) atmospheric deposition in the upper Columbia River basin. The latter possibility is supported by evidence from Arrow Lake upstream of Celgar, sediments of which had OCDD concentrations ranging from 26 to 68 pg/g and lower levels of OCDF (7.5 pg/g), but no other PCDDs/PCDFs at detection limits as low as 0.3 pg/g (Tuominen *et al.*, In Prep). Since there are no known or suspected point-sources of PCDD/PCDFs to Arrow Lake, this suggests their presence is due to atmospheric transport. This hypothesis is consistent with research showing that highly chlorinated PCDDs/PCDFs, especially OCDD, are associated with airborne particulate matter (Czuczwa *et al.*, 1984), and that these chemicals are widely distributed with aquatic sediments as the ultimate sinks (Czuczwa and Hites, 1986).

Comparison to Other Surveys

Environment Canada - 1990-1991

Environment Canada monitored PCDDs/PCDFs in SPM from three Columbia River sites -- one above Celgar and two below -- during October 1990, March 1991, and June 1991 (Table 6)(Tuominen *et al.*, 1994; Tuominen *et al.*, In Prep). Their initial monitoring at Waneta, just upstream of the Pend Oreille River, coincided with our original SPM collection. They also collected SPM from a site approximately 2.4 miles downstream of Celgar several days later (October 14-17, 1990). Unfortunately, low resolution GC/MS was employed for this initial survey, resulting in high detection limits (14-800 pg/g) and only one compound being detected: 2,3,7,8-TCDF at 1,900 pg/g (2.4 RM below Celgar) and at a mean concentration of 878 pg/g (Waneta). The difference in Environment Canada's 2,3,7,8-TCDF results at Celgar and Waneta may be due in part to deposition of sediments in this 30-mile river reach, but more likely reflects dilution from the Kootenay River (assuming no additional 2,3,7,8-TCDF inputs) which increases the Columbia River flow by an annual average of 75% between Celgar and Waneta (Butcher, 1992).

Subsequent monitoring of SPM by Environment Canada in 1991 showed an order of magnitude decrease in 2,3,7,8-TCDF and TEQ concentrations at both the Celgar and Waneta sites. This agrees well with PCDD/PCDF reductions reported by Celgar. The results also show that there is no significant contribution of PCDDs/PCDFs from the Columbia River above Celgar, represented by the Arrow Lake data.

Table 6. Summary of 2,3,7,8-TCDF and TEQ Concentrations in Columbia River SPM Analyzed by Environment Canada and Ecology, 1990-1991 (pg/g, dry weight basis).

Site	October 1990	March 1991	June 1991
Arrow Lake			

2,3,7,8-TCDF	U(4-11)	U(2)	U(1-1.4)
TEQ	0*	0.05*	0.04*
2.4 RM below Celgar			
2,3,7,8-TCDF	1,900	98	107*
TEQ	190	9.9	10.7*
Waneta			
2,3,7,8-TCDF	878*	≤0.4*	≤112*
TEQ	87.8*	0.04*	11.2*
Northport (Ecology)			
2,3,7,8-TCDF	99*	-	-
TEQ	10.8*	-	-

U=Undetected at or above range of quantitation limits in parentheses

TEQ=Toxicity Equivalent, based on detected values

*mean of two results

Although the Environment Canada data generally support results and conclusions from our early study (*e.g.* 2,3,7,8-TCDF as the major contributor to TEQ, substantial reductions in 2,3,7,8-TCDF discharges after 1990), the disagreement in 2,3,7,8-TCDF levels during concurrent monitoring by Ecology and Environment Canada is a confounding item. Tuominen *et al.* (1994) concluded that lower 2,3,7,8-TCDF concentrations obtained by Ecology are a result of incomplete mixing of the Pend Oreille River at Northport. Since the Pend Oreille contributes 27% of the mean annual Columbia River flow at the Canada border, 2,3,7,8-TCDF concentrations in our SPM sample should have been lowered accordingly when compared to Waneta, assuming identical TSS concentrations in the Pend Oreille, no additional 2,3,7,8-TCDF inputs, and complete mixing of the Pend Oreille River at Northport. However, if the Pend Oreille River is not completely mixed with the Columbia River at Northport, it stands to reason that 2,3,7,8-TCDF concentrations would be lowered to a greater degree since the Pend Oreille enters the Columbia at the left bank, the same side from which our samples were collected.

There is no direct evidence that the Pend Oreille and Columbia rivers are not completely mixed at Northport. The 10-mile reach between the confluence and Northport is free-flowing and rapid, often shallow and with a number of torturous bends, all suggesting good if not complete mixing. However, we have not found any empirical data on mixing and the results presented here are not adequate to assess the degree to which these rivers are mixed.

U.S. Geological Survey - 1992

USGS conducted a large-scale survey of sediment quality in Lake Roosevelt during 1992, results of which are reported in Bortleson *et al.* (1994). A portion of this survey involved sampling SPM concurrent with Ecology. Results of their 2,3,7,8-PCDD/PCDF analysis are shown in Table 7.

Table 7. Concentrations 2,3,7,8-PCDDs/PCDFs in Columbia River SPM at Northport Analyzed by the U.S. Geological Survey and Ecology During 1992 (pg/g, dry weight basis).

Compound	USGS-DWIS	USGS-SDPS	Ecology
2,3,7,8-TCDD	U(3.6)	U(3.7)	U(1.5-1.7)
1,2,3,7,8-PeCDD	U(4.4)	U(3.7)	U(1.0-1.5)
1,2,3,4,7,8-HxCDD	U(2.5)	U(4.9)	U(2.5-2.6)
1,2,3,6,7,8-HxCDD	U(8.6)	U(6.3)	U(3.2)
1,2,3,7,8,9-HxCDD	U(3.4)	U(5.4)	U(2.7)
1,2,3,4,6,7,8-HpCDD	210	U(37)	31*
OCDD	1,300	240	214*
2,3,7,8-TCDF	U(7.4)	U(9.4)	6.2*
1,2,3,7,8-PeCDF	U(4.6)	U(3.3)	U(1.7-1.8)
2,3,4,7,8-PeCDF	U(6.7)	U(4.5)	U(2.5-2.6)
1,2,3,4,7,8-HxCDF	U(7.4)	U(5.8)	U(2.2-2.6)
1,2,3,6,7,8-HxCDF	U(4.4)	U(6.3)	U(2.4-2.8)
2,3,4,6,7,8-HxCDF	U(8.0)	U(5.8)	U(2.2-2.5)
1,2,3,7,8,9-HxCDF	U(1.7)	U(6.3)	U(2.2-2.6)
1,2,3,4,6,7,8-HpCDF	130	U(18)	U(1.2-10)
1,2,3,4,7,8,9-HpCDF	U(6.1)	U(3.0)	U(1.0-10)
OCDF	230	130	U(11-14)
TEQ=	4.9	0.4	1.1

detected PCDDs/PCDFs in **bold** print

DWIS=Depth-Width Integrated Sample

SDPS=Short-Duration Point-Source Sample

U=Undetected at or above range of quantitation limits in parentheses

TEQ=Toxicity Equivalent, based on detected values

*mean of two results

Two SPM samples were analyzed for the USGS survey: a depth-width integrated sample (DWIS) collected at Northport during an 8.5-hour period on September 30, and sub-sample of our SPM which was collected during the same 8.5-hour period and designated as a short-duration point source (SDPS) sample. The purpose of this sampling scheme was to determine if PCDD/PCDF data obtained from a point source (*i.e.* from the left bank) were representative of PCDD/PCDF concentrations in the river cross-section.

The USGS samples had much higher concentrations of hepta- and octa-chlorinated congeners than ours, although the OCDD concentration in the SDPS sample agreed well with ours. The DWIS sample also had PCDD/PCDF concentrations at least 75% higher than SPM samples collected from the left bank, with the exception of 2,3,7,8-TCDF. It is possible that elevated PCDD/PCDF concentrations in the DWIS sample were due to Celgar's effluent, and that SPM samples from the left bank were sufficiently diluted by the Pend Oreille River (assuming incomplete mixing) to explain the difference. If this were the case, however, then detectable concentrations (*i.e.* ≥ 7.4 pg/g) of 2,3,7,8-TCDF would be expected in the DWIS since Celgar is probably the only upstream source of measurable 2,3,7,8-TCDF.

There is no clear explanation for the differences in PCDD/PCDF concentrations among these samples. Unfortunately, the USGS data do not support any conclusion about the degree of river mixing and the representativeness of point source data. If anything, these data underscore the high degree of variability associated with monitoring extremely low concentrations of contaminants in a large river.

Ecology Survey of Snake River SPM - 1996

EPA's TMDL for 2,3,7,8-TCDD in the Columbia River specifies three sub-basins for loading targets: the Columbia River above the international boundary, described in the present report; the Willamette River in Oregon; and the Snake River. These watersheds were selected for loading targets because each has a bleached kraft pulp mill which has been responsible for the majority of PCDD/PCDF loading in each basin.

Analysis of pulp mill effluents during a 1988 nationwide survey found that the Potlatch mill loaded 11.0 mg 2,3,7,8-TCDD/day to the Snake River (EPA, 1988 & 1990). The watershed target for the Snake River is 1.18 mg 2,3,7,8-TCDD/day at the mouth, which includes a waste load allocation of 0.39 mg 2,3,7,8-TCDD/day for the Potlatch mill. In addition, the average 2,3,7,8-TCDF load from Potlatch was estimated to be 50 mg/day.

Like Celgar, Potlatch initiated a number of changes, beginning around 1989, to reduce its production and discharge of PCDDs/PCDFs (EPA, 1990; Michael Letourneau, EPA, written communication). In 1996, we analyzed PCDDs/PCDFs in SPM collected from the mouth of the Snake River to determine the load of 2,3,7,8-TCDD and other PCDDs/PCDFs (Serdar and Cubbage, 1997). Five congeners were detected, generally at low concentrations (Table 8). Loads of 2,3,7,8-TCDD and 2,3,7,8-TCDF in 1996 represented reductions of 98% and 99%, respectively, when compared to loads measured during the 1988 survey of Potlatch effluent. Perhaps more notable is that the congener profile of PCDDs/PCDFs detected in the Snake River during 1996 shows many similarities to post-1990 Northport

SPM – OCDD and 1,2,3,4,6,7,8-HpCDD as the major congeners, low concentrations of 2,3,7,8-TCDF – possibly signaling a new PCDD/PCDF fingerprint from modernized bleached kraft pulp mills.

Table 8. Concentrations of 2,3,7,8-PCDDs/PCDFs in Snake River SPM During 1996 and Columbia River SPM, 1992-1994 (range; pg/g, dry weight basis).

Compound	SNAKE R. at Mouth (n=3)	Columbia R. at Northport (n=4)*
2,3,7,8-TCDD	U (0.24-0.32)	U(0.4-1.8)
1,2,3,7,8-PeCDD	U (0.23-0.29)	U(1.0) - 2.3
1,2,3,4,7,8-HxCDD	U (0.34-0.40)	U(0.6) - 1.5
1,2,3,6,7,8-HxCDD	U (1.1-1.3)	U(1.2) - 3.0
1,2,3,7,8,9-HxCDD	U (1.1-1.2)	U(0.5) - 3.2
1,2,3,4,6,7,8-HpCDD	22 - 27	3.5 - 74
OCDD	190 - 230	16.5 - 482
2,3,7,8-TCDF	2.0	1.1 - 6.2
1,2,3,7,8-PeCDF	U (0.19-0.23)	0.7 - 1.2
2,3,4,7,8-PeCDF	U (0.26-0.32)	U(0.3) - 0.6
1,2,3,4,7,8-HxCDF	U (0.42-0.48)	U(0.5) - 1.3
1,2,3,6,7,8-HxCDF	U (0.20-0.29)	0.6 - 1.0
2,3,4,6,7,8-HxCDF	U (0.53-0.58)	0.4
1,2,3,7,8,9-HxCDF	U (0.061-0.12)	U(0.4-2.6)
1,2,3,4,6,7,8-HpCDF	4.4 - 5.2 J	1.2 - 8.5
1,2,3,4,7,8,9-HpCDF	U (0.29-0.32)	U(0.7) - 0.9
OCDF	15 - 18	U(1.7) - 23.6
TEQ=	0.7	1.1 - 3.3

*n=5 for 2,3,7,8-TCDD and 2,3,7,8-TCDF

detected PCDDs/PCDFs in **bold print**

U=Undetected at or above range of quantitation limits in parentheses

J=estimated concentration

TEQ=Toxicity Equivalent, based on detected values

Conclusions

There was a significant decrease in the concentration of 2,3,7,8-TCDF bound to Columbia River SPM between 1990 and 1994. The decline in 2,3,7,8-TCDF concentrations was almost certainly due to pollution abatement efforts and process modifications at the Celgar pulp mill in Castlegar, B.C.

Congener profiles in SPM demonstrate substantial variation over time and do not appear to be directly related to discharges from Celgar. Aside from 2,3,7,8-TCDF, there was no clear trend in concentrations of SPM-bound PCDDs/PCDFs from 1990 to 1994.

The daily 2,3,7,8-TCDD load at Northport was well below the EPA TMDL watershed target (2.3 mg/day) during 1990 and 1994 monitoring. Theoretically, 2,3,7,8-TCDD loads may have slightly exceeded the target in 1992 and 1993, but this scenario was based on estimated *maximum possible* loads.

Recommendations

We recommend an additional round of SPM collection at Northport during low-flow conditions to:

- Determine if 2,3,7,8-TCDF concentrations remain low
- Find out if the congener profile has stabilized
- Check for the presence of 2,3,7,8-TCDD

Since the bulk of the PCDD/PCDF loads are apparently in the dissolved phase, analysis of the dissolved fraction should accompany future SPM analysis.

We also recommend collecting SPM during high-flow conditions to assess whether sediment resuspension contributes significant PCDD/PCDF loads to the upper Columbia River and Lake Roosevelt.

Any additional sampling should be accompanied by testing, using dye or other means, to determine the degree to which the Columbia and Pend Oreille rivers are mixed at Northport.

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